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C, H, and O Compounds Cycloprate, Kinoprene, Methoprene, and Resmethrin

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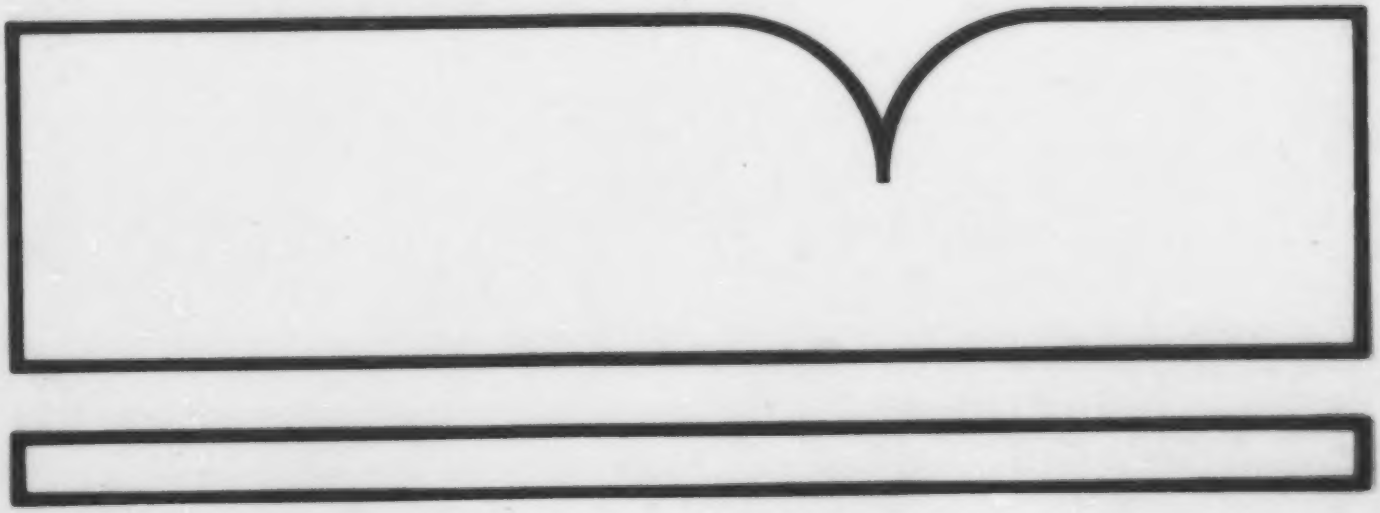

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C, H, AND O COMPOUNDS - CYCLOPRATE, KINOPRENE, METHOPRENE, AND RESMETHRIN

by

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16. ABSTRACT

A method was developed for the determination of four compounds containing only carbon, hydrogen, and oxygen (cycloprate, kinoprene, methoprene, and resmethrin), in wastewaters. The method development program consisted of a literature review; determination of extraction efficiency for each compound from water into methylene chloride; development of a deactivated silica gel cleanup procedure; and determination of suitable gas chromatographic and analysis conditions. Extraction and cleanup procedures were developed to provide 85 percent or greater recoveries of these compounds from the wastewater.

The final method was applied to Columbus POTW secondary effluent in order to determine the precision and accuracy of the method. The wastewater was spiked with the four compounds at levels of 100 µg/L and 1000 µg/L. Method detection limits (MDLs) for cycloprate, kinoprene, methoprene, and resmethrin in distilled water were 21 µg/L, 18 µg/L, 22 µg/L, and 36 µg/L, respectively.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid wastes.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report is one of a series that investigates the analytical behavior of selected pesticides and suggests a suitable test procedure for their measurement in wastewater. The method was modeled after existing EPA methods being specific yet as simplified as possible.

Robert L. Booth

Robert L. Booth, Acting Director
Environmental Monitoring and Support
Laboratory - Cincinnati

ABSTRACT

A method was developed for the determination of four compounds containing only carbon, hydrogen, and oxygen (cycloprate, kinoprene, methoprene, and resmethrin), in wastewaters. The method development program consisted of a literature review; determination of extraction efficiency for each compound from water into methylene chloride; development of a deactivated silica gel cleanup procedure; and determination of suitable gas chromatographic and analysis conditions. Extraction and cleanup procedures were developed to provide 85 percent or greater recoveries of these compounds from the wastewater. A packed column GC-FID analysis procedure was also developed.

The final method was applied to Columbus POTW secondary effluent in order to determine the precision and accuracy of the method. The wastewater was spiked with the four compounds at levels of 100 µg/L and 1000 µg/L. Recoveries for cycloprate, kinoprene, methoprene, and resmethrin at the 100 µg/L level were 84 ± 14 percent, 89 ± 6 percent, 93 ± 13 percent, and 86 ± 8 percent, respectively. Recoveries at the 1000 µg/L level were 94 ± 4 percent, 82 ± 6 percent, 90 ± 4 percent, and 91 ± 3 percent, respectively. Method detection limits (MDLs) for cycloprate, kinoprene, methoprene, and resmethrin in distilled water were 21 µg/L, 18 µg/L, 22 µg/L, and 36 µg/L, respectively. MDLs in wastewaters may be higher due to interfering compounds.

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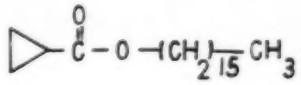
SECTION 1

INTRODUCTION

Cycloprate, kinoprene, methoprene, and resmethrin are neutral compounds containing only carbon, hydrogen, and oxygen. They were combined into one group for method development purposes only.

Little information was obtained from a literature survey for cycloprate (I).



I

The CAS registry number for cycloprate is 54460-46-7 and its IUPAC name is hexadecyl cyclopropanecarboxylate. Its common synonyms include "Zardex" and "ZR 856". Toxicity data and information on previously used analysis methods were not found during the literature search.

Kinoprene (II) is an insect growth regulator.

II

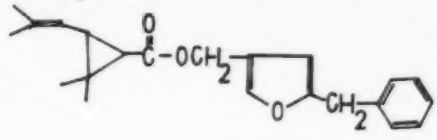
Its CAS registry number is 42588-37-4 and its IUPAC name is 2-propenyl (2E, 4E)-3,7,11-trimethyl-2,4-dodecadienoate. Common synonyms for kinoprene include "XR 777", "ENT 70531", "Enstar", and "ZR 77". Its LD50 is 4900 mg/kg in rats. No information on analysis methods used for kinoprene was found in the literature search.

Methoprene (III) is an insect growth regulator.

III

Its CAS registry number is 40596-69-8 and its IUPAC name is ethyl (2E, 4E) 3,7,11-trimethyldodeca-2,4-dienoate. Its common synonyms include "Entocon ZR-515", "Altosid", "Altosid CP-10", "Altosid PS-10", and "Altosid SR-10". The LD50 of methoprene is >34,600 mg/kg in rats. No analysis information was found in the literature search.

Resmethrin (IV) is a powerful insecticide.



IV

Its CAS registry number is 10453-86-8 and its IUPAC name is 5-benzyl-3-furylmethyl (1RS)-cis, trans-chrysanthemate. Common synonyms for resmethrin include "NIA 17370", "NRDC 104", "Penick 1382", "SBP 1382", and "Chryson". The LD50 for resmethrin is 4240 mg/kg in rats (1). An analysis method using extraction with ethyl ether/petroleum ether, cleanup on a Florisil column, and analysis by gas chromatograpy with a flame ionization detector (GC-FID) using a 10% SE-30 packed column was found in the literature (2).

The four compounds are neutral, observed to be stable in water, easily extracted from water, and contain only carbon, hydrogen, and oxygen. For these reasons, the selected approach to the determination of these compounds in water included extraction from water using separatory funnel techniques and methylene chloride as the extraction solvent, cleanup using silica gel adsorption chromatography, and analysis using packed column GC-FID. Standard concentration techniques using Kuderna-Danish (K-D) equipment were employed. The final method is included in Appendix A of this report.

SECTION 2

CONCLUSIONS

EXTRACTION AND CONCENTRATION

The four C, H, and O compounds can be extracted from water with greater than 90 percent recovery using standard separatory funnel extraction techniques with methylene chloride solvent. Use of K-D equipment to perform extract concentrations did not significantly affect compound recoveries.

CLEANUP

The C, H, and O compounds elute from six percent deactivated silica gel in 50 percent ethyl ether in petroleum ether with greater than 90 percent recovery. This was an effective cleanup procedure for Columbus POTW secondary effluent but was not assessed for any relevant wastewater samples.

CHROMATOGRAPHY

Two packed GC columns, 3% SP-2250 and 10% OV-210, were found to be acceptable for this application. The 3% SP-2250 column gave slightly better peak shape and was used as the primary column. The 10% OV-210 column was designated as the alternate column.

VALIDATION

In general, recoveries at concentration levels ranging from 50 to 2000 µg/L were acceptable (greater than 85 percent). The MDLs ranged from 18 to 36 µg/L; these values are slightly high due to the use of packed columns and the nonspecific flame ionization detector. Analytical curves constructed in the 50 to 2000 µg/L range were linear. Recoveries of the C, H, and O compounds from Columbus POTW secondary effluent were generally greater than 85 percent at the 100 and 1000 µg/L spike levels.

SECTION 3

EXPERIMENTAL

Studies were performed to determine if techniques such as separatory funnel extraction, silica gel adsorption chromatography cleanup, K-D apparatus concentration, and packed column GC-FID analysis would be applicable to the determination of cycloprate, kinoprene, methoprene, and resmethrin in wastewaters. Since recovery data and literature references indicated that these compounds are relatively stable in water, stability studies were not performed.

EXTRACTION AND CONCENTRATION

One liter of sample water was placed in a two-liter separatory funnel and the pH was buffered at 6.8 by addition of two grams each of monobasic sodium phosphate and dibasic sodium phosphate. The sample was then spiked with 100 µg/L of the four compounds and extracted three times each with 60 mL of methylene chloride. The combined extracts were dried by passing them through 10 cm of anhydrous granular sodium sulfate and concentrated to one milliliter.

CLEANUP

A 20-gram silica gel column (six percent deactivated with water) was prepared with 50 mL of petroleum ether suspended over it. The four compounds, 100 µg each dissolved in five mL of methylene chloride, were added to the above mentioned petroleum ether. This solvent plus an additional 50 mL of petroleum ether were eluted from the column and collected (F1). Nine additional 25-mL solvent elutions were collected: six percent ethyl ether in petroleum ether (F2); 15 percent ethyl ether in petroleum ether (F3); 50 percent ethyl ether in petroleum ether (F4); ethyl ether (F5); six percent acetone in ethyl ether (F6); 15 percent acetone in ethyl ether (F7); 50 percent acetone in ethyl ether (F8); acetone (F9); and six percent methanol in acetone (F10). Each fraction was concentrated to five mL and further concentrated to one mL after addition of 20 mL of methyl t-butyl ether.

The above mentioned experiment was repeated, but only two fractions were collected. The first fraction was the same as F1 above and the second fraction was obtained by eluting with 100 mL of 50 percent ethyl ether in petroleum ether. Fractions were again concentrated to one mL after substituting the solvent with methyl t-butyl ether.

CHROMATOGRAPHY

Two columns were evaluated for the determination of the four C, H, and O compounds: 3% SP-2250 on 100/120 mesh Supelcoport and 10% OV-210 on 100/120 mesh Supelcoport.

VALIDATION STUDIES

The MDLs for the four compounds were determined by analyzing seven replicate distilled water samples spiked at the 50 µg/L concentration level. The sample extracts were cleaned up using the silica gel cleanup procedure prior to analysis. The amounts recovered were determined by external standard calibration and the MDLs were calculated from these data.

Distilled water was also spiked in duplicate at the 50, 100, 500, 1000, and 2000 µg/L concentration levels and recoveries of the four compounds were determined as described earlier. An analytical curve was generated by plotting the amount spiked into the samples versus the amount recovered from the samples.

A relevant wastewater was not available for these four compounds, and Columbus POTW secondary effluent was used for wastewater validation studies. Seven replicates of the wastewater were analyzed to determine the background levels. The wastewater was spiked with the four compounds at the 100 and 1000 µg/L concentration levels, processed and analyzed. Seven replicate extractions were performed at each concentration level.

SECTION 4

RESULTS AND DISCUSSION

EXTRACTION AND CONCENTRATION

Cycloprate, kinoprene, methoprene, and resmethrin were extracted from distilled water with 90 percent or better extraction efficiency using standard separatory funnel techniques and methylene chloride extraction solvent. Recovery data from duplicate extractions at the 100 µg/L concentration level are given in Table 1.

TABLE 1. EXTRACTION OF C, H, AND O COMPOUNDS FROM WATER

Compound	Percent Recovery (a)
Cycloprate	110, 94
Kinoprene	93, 110
Methoprene	97, 100
Resmethrin	90, 96

(a) Results from duplicate extractions at the 100 µg/L concentration level.

CLEANUP

The four compounds primarily eluted in silica gel fractions two and three (six percent ethyl ether in petroleum ether and 15 percent ethyl ether in petroleum ether). Greater than 90 percent recovery was achieved for all four compounds. Elution order and recovery data are given in Table 2.

The above mentioned experiment was repeated, however, only fractions one and four were collected. In order to simplify the cleanup procedure and obtain all four compounds in one fraction, the elution scheme was revised to use elution with 100 mL of 50 percent ethyl ether in petroleum ether to replace the elutions that gave fractions 2, 3, and 4. With the revised elution scheme recoveries for all four compounds were 95 percent of greater. The recovery data are given in Table 3.

TABLE 2. ELUTION ORDERS OF C, H, AND O COMPOUNDS FROM SILICA GEL

Compound	Recovery in Given Fraction, %(a) F1	F2	F3	F4	Total
Cycloprate	ND(b)	97	ND	ND	97
Kinoprene	ND	100	ND	ND	100
Methoprene	ND	ND	101	<1	101
Resmethrin	ND	65	27	ND	92

(a) Compounds spiked at the 100 µg/L level; single determination.

F1 = 50 mL petroleum ether plus sample in five milliliters of methylene chloride; 25 mL petroleum ether wash
F2 = 50 mL six percent ethyl ether in petroleum ether
F3 = 50 mL 15 percent ethyl ether in petroleum ether
F4 = 50 mL 50 percent ethyl ether in petroleum ether

(b) Not detected.

TABLE 3. RECOVERIES OF C, H, AND O COMPOUNDS FROM SILICA GEL

Compound	Percent Recovery(a)(b)
Cycloprate	96
Kinoprene	99
Methoprene	98
Resmethrin	95

(a) Compounds spiked at the 100 µg/L level; single determination.
(b) 100 mL of 50 percent ethyl ether in petroleum ether was used as the elution solvent.

CHROMATOGRAPHY

Both the 3% SP-2250 and 10% OV-210 columns were satisfactory for the determination of the four C, H, and O compounds. The 3% SP-2250 column, however, gave slightly better peak shape and was chosen as the primary column. The following conditions were used for the primary column:

Column:	2m x 2.0mm ID 3% SP-2250 on 100/120 mesh Supelcoport
Detector:	Flame ionization
Injector Temperature:	280°C
Detector Temperature:	300°C
Oven Temperature:	Programmed from 180°C to 240°C at 8 C/min
Carrier Gas:	Helium at 30 mL/min

A chromatogram obtained under these conditions is shown in Figure 1.

The following conditions were used for the alternate column:

Column:	2m x 2.0mm ID 10% OV-210 on 100/120 mesh Supelcoport
Detector:	Flame ionization
Injector Temperature:	280°C
Detector Temperature:	300°C
Oven Temperature:	Programmed from 180°C to 240°C at 4°C/min.
Carrier gas:	Helium at 30 mL/min.

A chromatogram obtained under these conditions is shown in Figure 2.

VALIDATION STUDIES

The MDLs for these compounds ranged from 18 to 36 µg/L. These MDLs are higher than is normally acceptable, due to the use of packed columns and FID. Recoveries and MDL data from these studies are given in Table 4.

TABLE 4. DATA FROM MDL DETERMINATION OF THE C, H, AND O COMPOUNDS.

Compound	Amount Spiked, µg/L	Amount Recovered, µg/L(a)	MDL, µg/L
Cycloprate	50	54 ± 6.8	21
Kinoprene	50	52 ± 5.7	18
Methoprene	50	48 ± 7.0	22
Resmethrin	50	49 ± 11	36

(a) Average of seven replicates.

Recoveries obtained during the analytical curve studies were greater than 90 percent for all four compounds at all five concentration levels. Recoveries for the four compounds are given in Table 5. The analytical curves generated for the four compounds were linear (correlation coefficients greater than 0.996) and are shown in Figures 3-6.

TABLE 5. DATA FROM ANALYTICAL CURVE DETERMINATION FOR THE C, H, AND O COMPOUNDS

	Amount Recovered at Given Spike Level, µg/L(a)				
Compound	50	100	500	1000	2000
Cycloprate	54	96	500	1000	1800
Kinoprene	52	98	450	960	2100
Methoprene	48	94	460	960	2100
Resmethrin	49	99	450	990	2100

(a) Average of duplicate analyses.

Recoveries of the four compounds from Columbus POTW secondary effluent were greater than 85 percent except at the 100 µg/L level for kinoprene (84 percent) and 1000 µg/L level for methoprene (82 percent). These lower recoveries were presumably due to the variability of the method. Recovery data for the determination of the C, H, and O compounds from wastewater are presented in Table 6. A chromatogram of the wastewater spiked at the 100 µg/L level is shown in Figure 7. No interferences were observed in the unspiked wastewaters.

TABLE 6. RECOVERIES FROM VALIDATION OF C, H, AND O COMPOUNDS

Compound	Spike Level, µg/L	Recovery, %(a)	Percent Relative Standard Deviation
Kinoprene	100	84	14
	1000	94	4
Methoprene	100	89	6
	1000	82	6
Cycloprate	100	93	13
	1000	90	4
Resmethrin	100	86	8
	1000	91	3

(a) Average of seven replicate analyses in Columbus POTW.

REFERENCES

1. Berteau, P.E., and W.A. Dean. A Comparison of Oral and Inhalation Toxicities of Four Insecticides to Mice and Rats. Bull. Environ. contam. Toxicol., 19(1):113:120, 1978.

2. Mestres, R., S. Atmawijaya, and C. Chevallier. Methode de Recherche et de Dosage des Residus de pesticides dans les Produits Cerealiers. Ann. Fals. Exp. Chim., 72(780): 577-589, 1979.

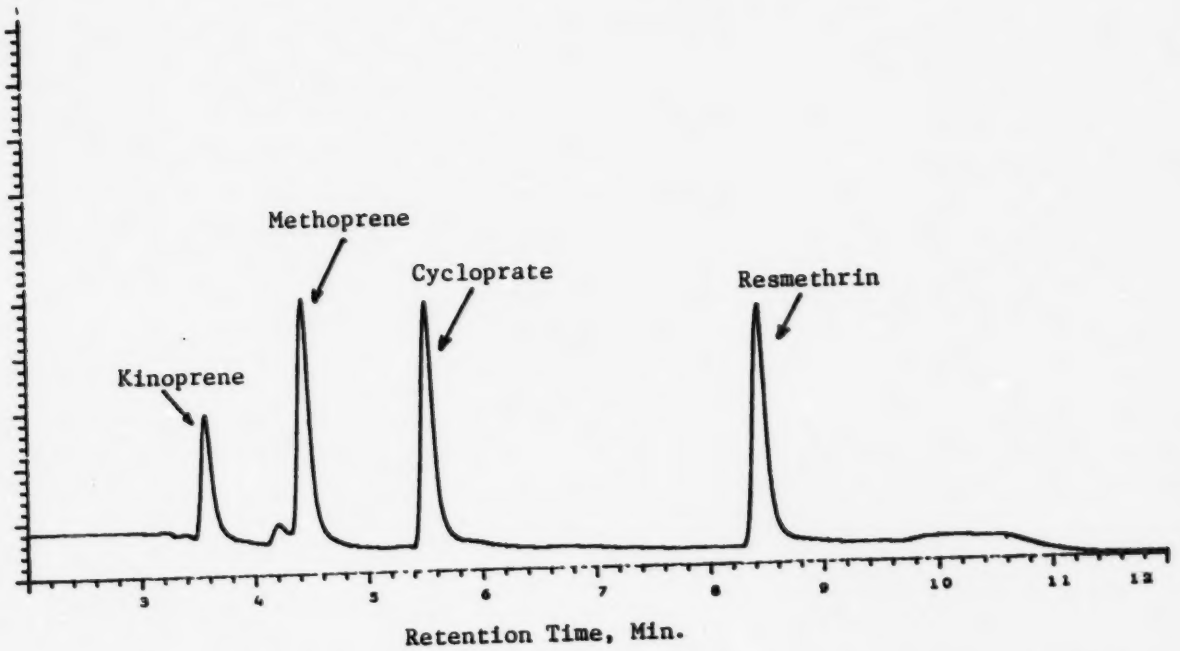


Figure 1. GC-FID Chromatogram of 200 ng Each of C, H, and O Compounds (Column 1)

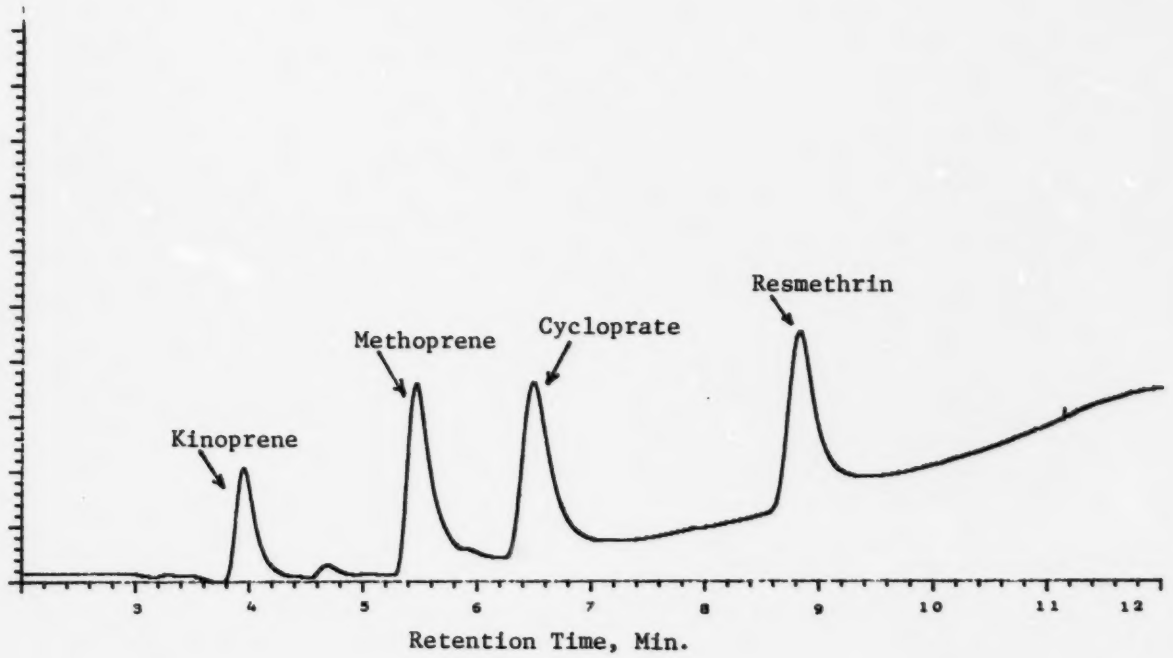


Figure 2. GC-FID Chromatogram of 200 ng Each of C, H, and O Compounds (Column 2)

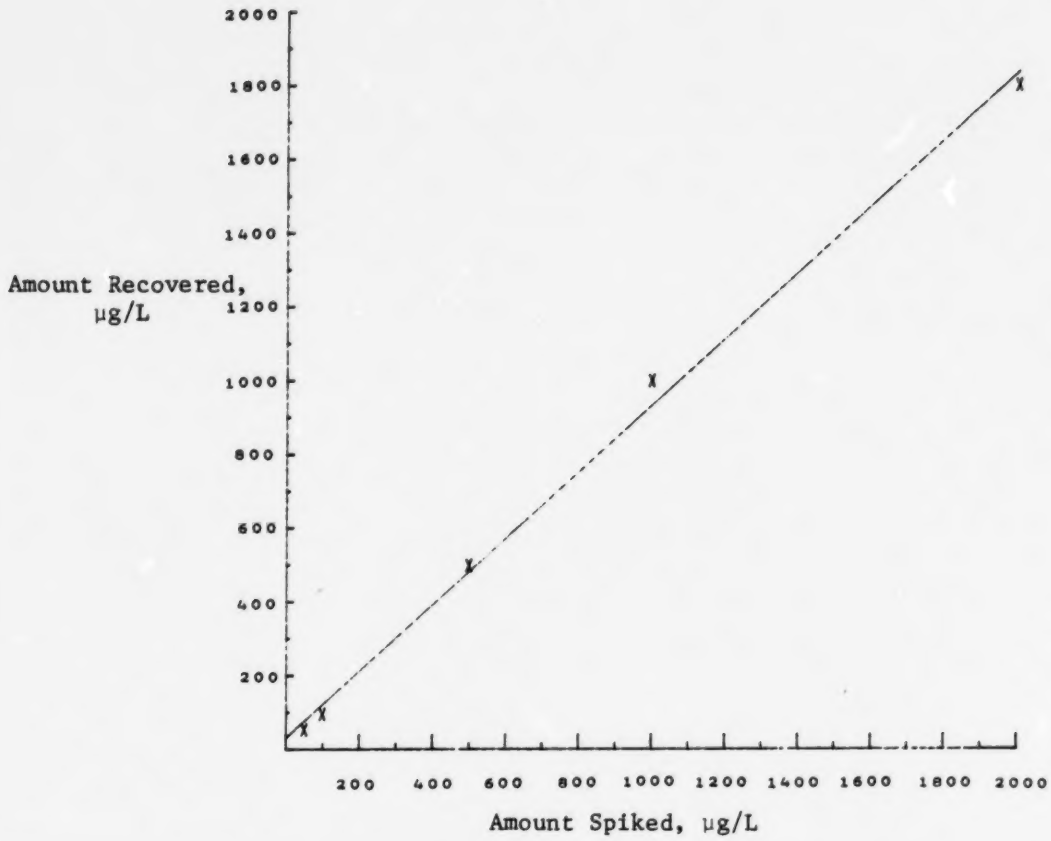


Figure 3. Analytical Curve for Cycloprate.

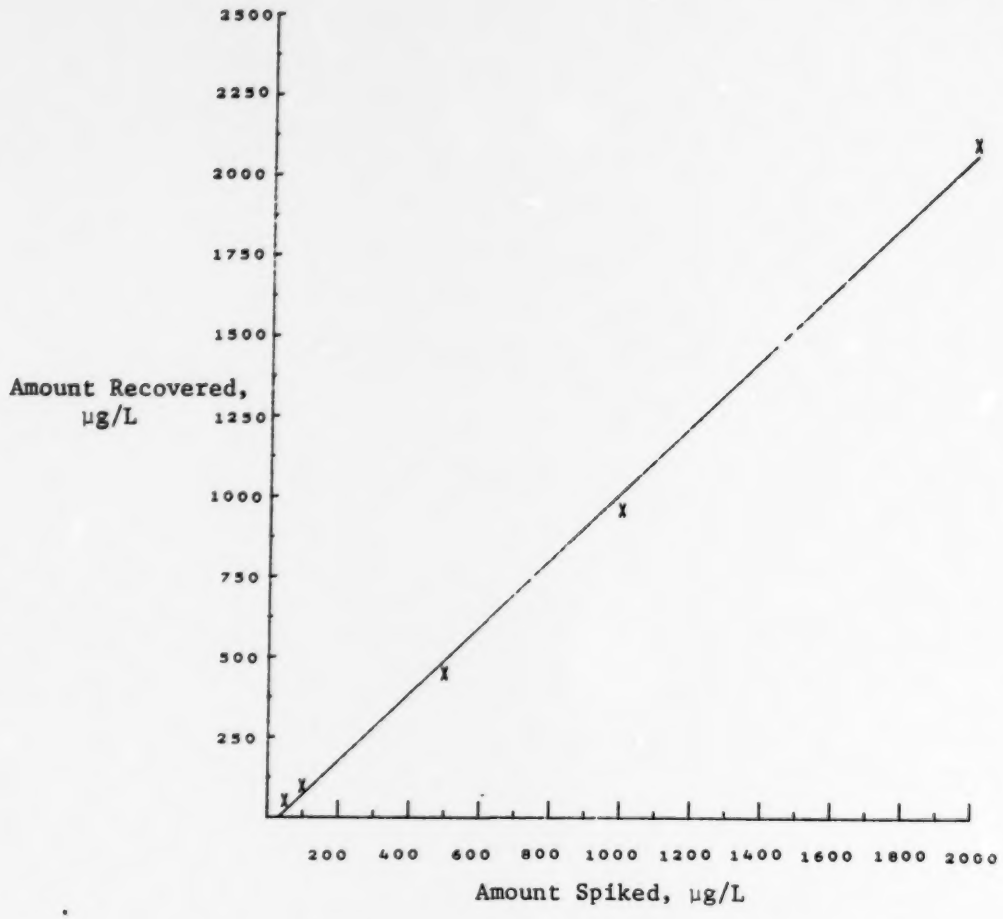


Figure 4. Analytical Curve for Kinoprene

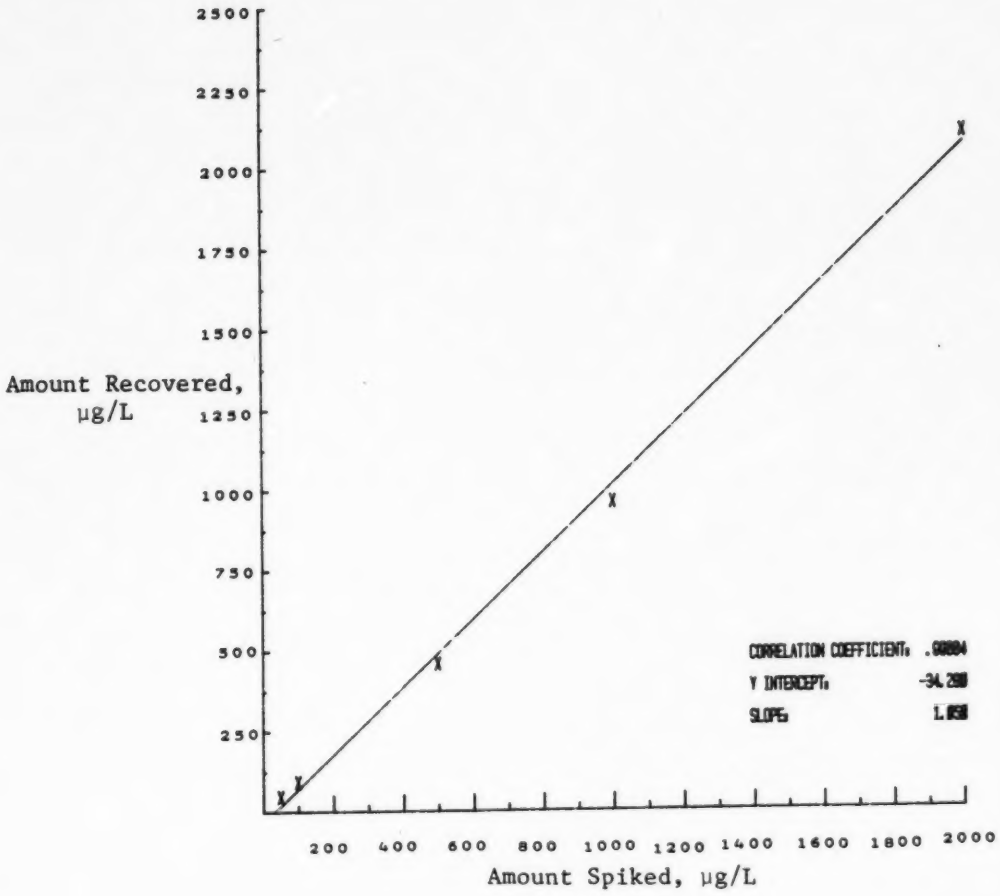


Figure 5. Analytical Curve for Methoprene

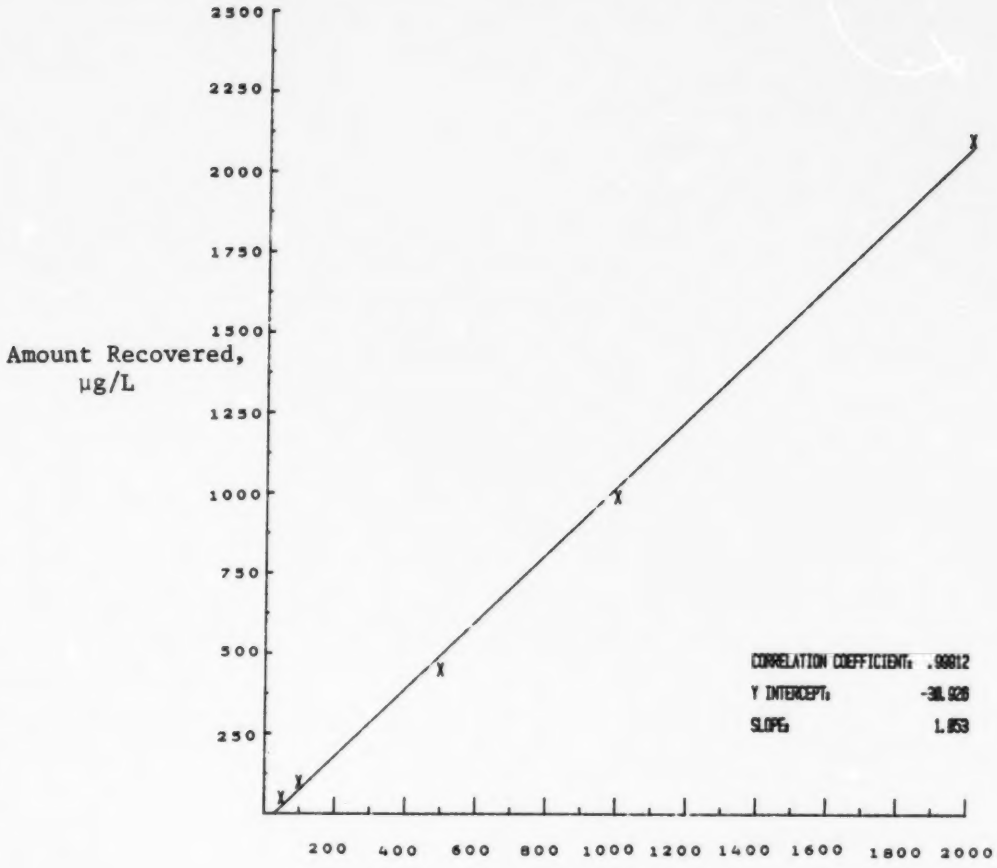


Figure 6. Analytical Curve for Resmethrin.

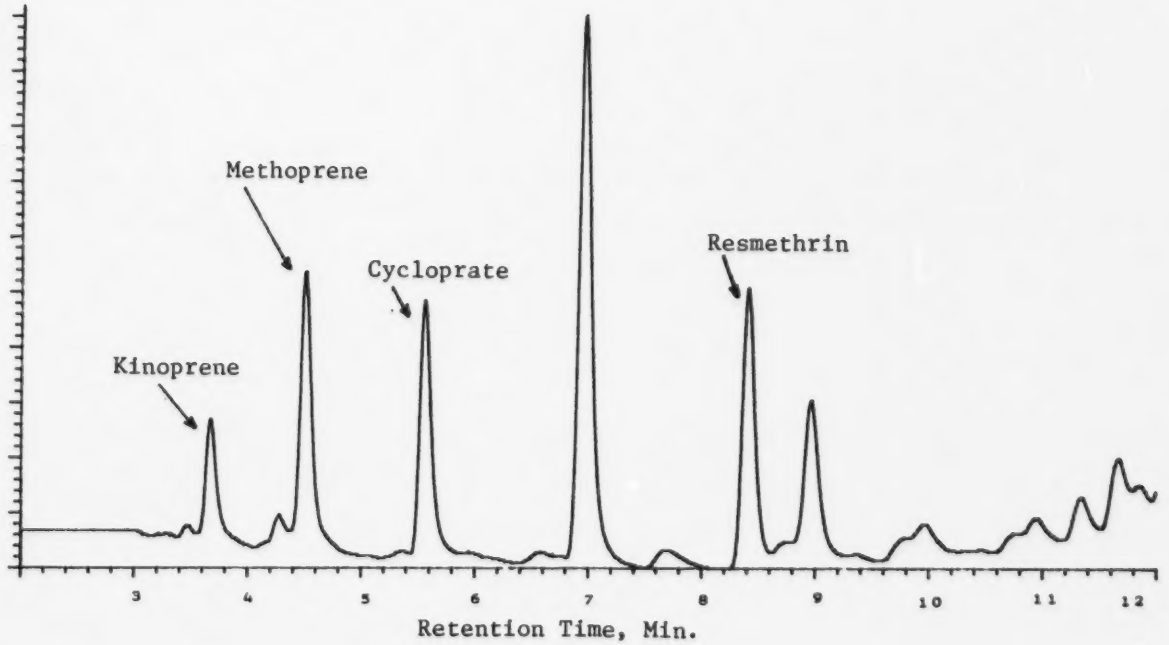


Figure 7. GC-FID Chromatogram of Columbus POTW Secondary Effluent Spiked at the 100 µg/L Level.

C, H, AND O COMPOUNDS

METHOD 616

1. Scope and Application

1.1 This method covers the determination of certain carbon-, hydrogen-, and oxygen-containing pesticides. The following parameters can be determined by this method:

Parameter	CAS No.
Cycloprate	54460-46-7
Kinoprene	42588-37-4
Methoprene	40596-69-8
Resmethrin	10453-86-8

1.2 This is a gas chromatgraphic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. Any modification of this method beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.3 The method detection limit (MDL, defined in Section 15) for each parameter is listed in Table 2. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 The sample extraction and concentration steps in this method are essentially the same as certain other 600 series methods. Thus, a single sample may be extracted to measure the compounds included in the scope of the methods. When cleanup is required, the concentration levels must be high enough to permit selecting aliquots, as necessary, in order to apply appropriate cleanup procedures.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

1.6 When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Section 14 provides gas chromatograph/mass spectrometer (GC-MS) criteria appropriate for the qualitative confirmation of compound identifications.

2. Summary of Method

2.1 A measured volume of sample, approximately 1 liter, is solvent extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and concentrated to 1.0 mL. Gas chromatographic conditions are described which permit the separation and measurement of the compounds in the extract by flame ionization detector gas chromatography (GC-FID).[1]

2.2 This method provides a silica gel column cleanup procedure to aid in the elimination of interferences which may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis

by running laboratory reagent blanks as described in Section 8.5.

3.1.1 Glassware must be scrupulously cleaned.[2] Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 4 hours. Do not heat volumetric ware. Some thermally stable materials such as PCBs may not be eliminated by this treatment. Thorough rinsing with acetone and pesticide quality hexane may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality sampled. The cleanup procedure in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 2.

4. Safety

4.1 The toxicity of carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential

health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[3-5] for the information of the analyst.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle - Amber borosilicate or flint glass, 1-liter or 1-quart volume, fitted with screw caps lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional) - Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated at 4 C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.)

5.2.1 Separatory funnel - 2000 mL, with Teflon stopcock.

5.2.2 Drying column - Chromatographic column 400 mm long x 10 mm ID with coarse frit.

5.2.3 Chromatographic column - 400 mm long x 19 mm ID with 250 mL reservoir at the top and Teflon stopcock (Kontes K-420290 or equivalent).

5.2.4 Concentrator tube, Kuderna-Danish - 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. A ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative flask, Kuderna-Danish - 250 mL (Kontes K-570001-0250 or equivalent). Attach to concentrator or tube with springs.

5.2.6 Snyder column, Kuderna-Danish - three ball macro (Kontes K-503000-0121 or equivalent).

5.2.7 Snyder column, Kuderna-Danish - two-ball micro (Kontes K-569001-0219 or equivalent).

5.2.8 Vials - Amber glass, 10 to 15 mL capacity with Teflon lined screw-cap.

5.2.9 Graduated cylinder - 1000-mL

5.2.10 Erlenmeyer flask - 250-mL

5.3 Boiling chips - approximately 10/40 mesh carborundum. Heat at 400°C for 4 hours or Soxhlet extract with methylene chloride.

5.4 Water bath - Heated, capable of temperature control ($\pm$2°C). The bath should be used in a hood.

5.5 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

5.6 Gas chromatoraph - Analytical system complete with gas

chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column 1 - 180 cm long x 2 mm ID glass, packed with 3% SP2250 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 15 Alternate columns may be used in accordance with the provisions described in Section 12.1.

5.6.2 Column 2 - 180 cm long x 2 mm ID glass, packed with 10% OV-210 on Supelcoport (100/120 mesh) or equivalent.

5.6.3 Detector - Flame ionization detector (FID). This detector has proven effective in the analysis of wastewaters for the compounds listed in the scope and was used to develop the method performance statements in Section 15.

6. Reagents

6.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

6.2 Methylene chloride, methanol, petroleum ether, ethyl ether, methyl t-butyl ether, distilled-in-glass quality or equivalent. Ethyl ether must be free of peroxides as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips.

6.3 Sodium sulfate (ACS) Granular, anhydrous; heated in a muffle furnace at 400°C overnight.

6.4 Silica gel - Davison Grade 923 (100/120 mesh). Purchase activated. To prepare for use, place in a wide-mouth

jar and heat overnight at 120-130°C. Seal tightly with Teflon or aluminum foil-lined screw cap and cool to room temperature.

6.5 Sodium phosphate, monobasic, monohydrate.

6.6 Sodium phosphate, dibasic.

6.7 Stock standard solutions (1.00 µg/µL) - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams of pure material. Dissolve the material in distilled-in-glass quality methyl t-butyl ether and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Frequently check standard solutions for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Stock standard solutions must be replaced after six months or sooner if comparison with check standards indicates a problem.

7. Calibration

7.1 Establish gas chromatographic operating parameters equivalent to those indicated in Table 2. The gas chromatographic system can be calibrated using the

external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 For each compound of interest, prepare calibration standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with methyl t-butyl ether. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the range of concentrations expected in the sample concentrations or should define the working range of the detector.

7.2.2 Using injection of 1 to 5 µL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each compound at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, the average calibration factor can be used in place of a calibration curve.

7.2.3 The working calibration curve or calibration factor must be verified on each working shift by the measurement of one or more calibration standards If the response for any compound varies from the predicted response by more than 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration

factor must be prepared for that compound.

7.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each compound of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with methyl t-butyl ether. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations expected in the sample concentrates or should define the working range of the detector.

7.3.2 Using injections of 1 to 5 µL of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the compound to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard in µg/L.

C_s = Concentration of the compound to be measured in µg/L.

If the RF value over the working range is constant less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve or response ratios, A_s/A_{is} against RF.

7.3.3 The working calibration curve or RF must be verified on each working shift by the measurement of one or more calibration standards. If the response for any compound varies from the predicted response by more than 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.4 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory using this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or

lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a representative spike concentration for each compound to be measured. Using stock standards, prepare a quality control check sample concentrate in methyl t-butyl ether 1000 times more concentrated than the selected concentrations.

8.2.2 Using a pipet, add 1.00 mL of the check sample concentrate to each of a minimum of four 1000-mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery (R), and the standard deviation of the percent recovery (s), for the results. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using the appropriate data from Table 3, determine the recovery and single operator precision expected for the method, and compare these results to the values measured in Section 8.2.3. If the data are not comparable, the analyst must review potential problem areas and repeat the test.

8.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance as follows:

Upper Control Limit (UCL) = $R + 3s$

Lower Control Limit (LCL) = $R - 3s$

where R and s are calculated as in Section 8.2.3. the UCL and LCL can be used to construct control charts[6] that are useful in observing trends in performance.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as $R \pm s$. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternatively, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly[6].

8.4 The laboratory is required to collect in duplicate a portion of their samples to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for a particular compound does not fall within the control limits for method performance, the results reported for that compound in all samples processed as part of the same set must be qualified as described in Section 13.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Before processing any samples, the analyst should demonstrate through the analysis of a 1-liter aliquor of reagent water that all glassware and reagents interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. Samples Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices[7] should be followed; however, the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of plastic and other potential sources of contamination.

9.2 The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

9.3 Adjust the pH of the sample to 6.8 by addition of 2 g each of monobasic and dibasic sodium phosphate per liter of sample.

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-liter separatory funnel. Add 2g each of monobasic sodium phosphate and dibasic sodium phosphate to the sample to adjust the pH to 6.8.

10.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 250-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride

to complete the quantitative transfer. Once the flask rinse has passed through the drying column, rinse the column with 30 to 40 mL of methylene chloride.

10.6 Add 1 or 2 clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath, 60 to 65°C, so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3-4 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.7 Remove the macro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. Adjust the sample extract volume to 5 mL with methylene chloride.

10.8 Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extract is to be stored longer than two days, transfer the extract to a screw capped vial with a Teflon-lined cap. If the sample extract requires no further cleanup, proceed to step 10.9. If the sample requires cleanup, proceed to Section 11.

10.9 Add 1 or 2 boiling chips and attach a two-ball micro-Snyder column to the concentrator tube. Prewet the micro-Snyder column with methylene chloride and concentrate the solvent extract to 1 mL as before.

10.10 Add 20 mL of methyl t-butyl ether to the concentrator tube and reconcentrate the solvent extract as before. When an apparent voume of 0.5 mL is reached, or the solution stops boiling, remove the K-D apparatus and allow it to drain and cool for 10 minutes.

10.11 Remove the micro-Snyder column and adjust the volume of the extract to 1.0 mL with methyl t-butyl ether. Transfer the extract to an appropriate container for subsequent GC analysis.

10.12 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedure recommended in this method has been used for the analysis of various clean waters and industrial effluents. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each compound of interest is no less than 85%.

11.2 The following silica gel column cleanup procedure has been demonstrated to be applicable to the four C, H, and O pesticides listed in Table 1.

11.2.1 Deactivate silica gel by mixing 100 mL of acetone, 1.2 mL of distilled water and 20 g of silica gel thoroughly for 30 minutes in a 250-mL beaker. Transfer the slurry to a chromatographic column (silica gel is retained with a plug of glass wool). Allow the solvent to elute from the column until the silica gel is almost exposed to the air. Wash the column sequentially with 10 mL of acetone, two 10-mL portions of methylene chloride, and three 10-mL portions of petroleum ether. Use a column flow rate of 2 to 2.5 mL/min throughout the wash and elution profiles. Add an additional 50 mL of petroleum ether to the head of the column.

11.2.2 Quantitatively add the methylene chloride extract from Section 10.8 to the head of the column. Allow the solvent to elute from the column until the silica gel is almost exposed to the air. Elute the column with 25 mL of petroleum ether. Discard this fraction.

11.2.3 Elute the column with 50 mL of 6% ethyl ether in petroleum ether (Fraction 1) and collect eluate in a K-D apparatus. Repeat process with 50 mL of 15% ethyl ether in petroleum ether (Fraction 2), add 100 mL of 50% ethyl ether in petroleum ether (Fraction 3). Collecting each fraction in a separate K-D apparatus. The elution patterns for the C, H, and O pesticides are shown in Table 1. Concentrate each fraction to 1 mL as described in Sections 10.9, 10.10 and 10.11. Proceed with gas chromatographic analysis.

11.2.4 The above-mentioned fractions can be combined before concentration at the discretion of the analyst.

12. Gas Chromatography

12.1 Table 2 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are estimated retention times and method detection limits that can be achieved by this method. Examples of the separations achieved by Column 1 and Column 2 are shown in Figure 1 and 2. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met. Capillary (open-tublar) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Section 8.2 are met.

12.2 Calibrate the gas chromatographic system daily as described in Section 7.

12.3 If the internal standard approach is being used, the analyst must not add the internal standard to the sample extracts until immediately before injection into the instrument. Mix thoroughly.

12.4 Inject 1 to 5 µL of the sample extract using the solvent flush technique[8]. Record the volume injected to the nearest 0.05 µL, and the resulting peak sizes in area or peak height units. An automated system that consistently injects a constant volume of extract may also be used.

12.5 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for the peak exceeds the working range of the system, dilute the extract ad reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration in the sample can be calculated as follows:

$$\text{Concentration, } \mu g/L = \frac{(A)(V_t)}{(V_i)(V_s)}$$

where:

A = Amount of material injected, in nanograms.

V_i = Volume of extract injected in µL.

V_t = Volume of total extract in µL.

V_s = Volume of water extracted in mL.

13.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 as follows:

$$\text{Concentration, } \mu g/L = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Response for the compound to be measured.

A_{is} = Response for the internal standard.

I_s = Amount of internal standard added to each extract in µg.

V_o = Volume of water extracted, in liters.

13.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.3 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in Section 8.3, data for the affected compounds must be labeled as suspect.

14. GC-MS Confirmation

14.1 It is recommended that GC-MS techniques be judiciously employed to support qualitative identifications made with this method. The mass spectrometer should be capable

of scanning the mass range from 35 amu to a mass 50 amu above the molecular weight of the compound. The instrument must be capable of scanning the mass range at a rate to produce at least 5 scans per peak but not to exceed 7 seconds per scan utilizing a 70-V (nominal) electron energy in the electron impact ionization mode. A GC to MS interface constructed of all-glass or glass-lined materials is recommended. When using a fused silica capillary column, the column outlet should be threaded through the interface to within a few mm of the entrance to the source ionization chamber. A computer system should be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program.

14.2 Gas chromatographic columns and conditions should be selected for optimum separation and performance. The conditions selected must be compatible with standard GC-MS operating practices. Chromatographic tailing factors of less than 5.0 must be achieved.[10]

14.3 At the beginning of each day that confirmatory analyses are to be performed, the GC-MS system must be checked to see that all DFTPP performance criteria are achieved.[9]

14.4 To confirm an identification of a compound, the background corrected mass spectrum of the compound must be obtained from the sample extract and compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. It is recommended that at least 25 nanograms of material be injected into the GC-MS. The criteria below must be met for qualitative confirmation.

14.4.1 The molecular ion and all other ions that are present above 10% relative abundance in the mass be present in the mass spectrum of the sample with agreement to plus or minus 10%. For example, if the relative abundance of an ion is 30% in the mass spectrum of the standard, the allowable limits for the relative abundance of that ion in the mass spectrum for the sample would be 20-40%.

14.4.2 The retention time of the compound in the sample must be within 6 seconds of the same compound in the standard solution.

14.4.3 Compounds that have very similar mass spectra can be explicitly identified by GC-MS only on the basis of retention time data.

14.5 Where available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

14.6 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These may include the use of alternate packed or capillary GC columns or additional cleanup (Section 11).

15. Method Performance

15.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.[11] The MDL concentrations listed in Table 2 were obtained using reagent water.[1] Similar results were achieved using representative wastewaters.

15.2 This method has been tested for linearity of recovery from spiked reagent water and has been demonstrated to be applicable over the concentration range 10 x MLD to 1000 x MDL.

15.3 In a single laboratory, Battelle Columbus Laboratories, using spiked wastewater samples, the average recoveries presented in Table 3 were obtained after silica gel cleanup. Seven replicates of each of two different wastewaters were spiked and analyzed. The standard deviation of the percent recovery is also included in Table 3.[1]

REFERENCES

1. "Development of Methods for Pesticides in Wastewater," Report for EPA Contract 68-03-2956 (In preparation).

2. ASTM Annual Book of Standards, Part 31, D3694, "Standard Practice for Preparation of Sample Containers and for" Preservation," American Society for Testing and Materials, Philadelphia, PA, p. 679, 1980.

3. "Carcinogens - Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August, 1977.

4. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

5. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

6. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, U.S. Environmental Protection Aency, Environemtnal Monitoring and Support Laboratory - Cincinnati, Ohio 45268, March 1979.

7. ASTM Annual Book of Standards, Part 31, D3370, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, p. 76, 1980.

8. Burke, J. A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037 (1965).

9. Eichelberger, J. W., Harris, L. E., and Budde, W. L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography - Mass Spectrometry," Analytical Chemistry, 47, 995 (1975).

10. McNair, H. M. and Bonelli, E. J., "Basic Chromatography", Consolidated Printing, Berkeley, California, p. 52 (1969).

11. Glaser, J. A. et al, "Trace Analysis for Wastewaters", Environmental Science and Technology, 15, 1426 (1981)

TABLE 1. ELUTION CHARACTERISTICS OF THE C, H, AND O COMPOUNDS FROM 6% DEACTIVATED SILICA GEL

Parameter	Recovery in Specified Fraction(a)			
	F1	F2	F3	Total
Cycloprate	97	ND(a)	ND	97
Kinoprene	100	ND	ND	100
Methoprene	ND	101	<1	101
Resmethrin	65	27	ND	92

(a) Elution solvents are 50 mL each of the following:
F1 = 6% ethyl ether in petroleum ether
F2 = 15% ethyl ether in petroleum ether
F3 = 50% ethyl ether

(b) ND = Not detected.

TABLE 2. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention Time (Min.) Column 1	Column 2	MDL (µg/L)
Cycloprate	3.6	3.9	21
Kinoprene	4.4	5.5	18
Methoprene	5.5	6.5	22
Resmethrin	8.4	8.9	36

Column 1 conditions: Supelcoport (100/120 mesh) coated with 3% SP-2250 packed in a 1.8 m long x 2 mm ID glass column with helium carrier gas at a flow rate of 30 mL/min. Column temperature is programmed from 180°C to 240°C at 8°C/min., injector temperature is 280°C and detector is 300°C. A flame ionization detector is used.

Column 2 conditions: Supelcoport (100/120 mesh) coated with 10% OV-210 packed in a 1.8 m long x 2 mm ID glass columns with helium carrier gas at a flow rate of 30 mL/min. Column temperature is programmed from 180°C to 240°C at 4°C/min., injector temperature is 280°C and detector is 300°C. A flame ionization detector is used.

TABLE 3. SINGLE LABORATORY ACCURACY AND PRECISION(a)

Parameter	Sample Type(b)	Background µg/L(c)	Spike µg/L	Mean Recovery %	Standard Deviation %	Number of Replicates
Cycloprate	1	ND	100	84	14	7
	1	ND	1000	94	4	7
Kinoprene	1	ND	100	89	6	7
	1	ND	1000	82	6	7
Methoprene	1	ND	100	93	13	7
	1	ND	1000	90	4	7
Resmethrin	1	ND	100	86	8	7
	1	ND	1000	91	3	7

(a) Column 1 conditions were used.

(b) 1 = Columbus POTW secondary effluent.

(c) ND = Not detected.

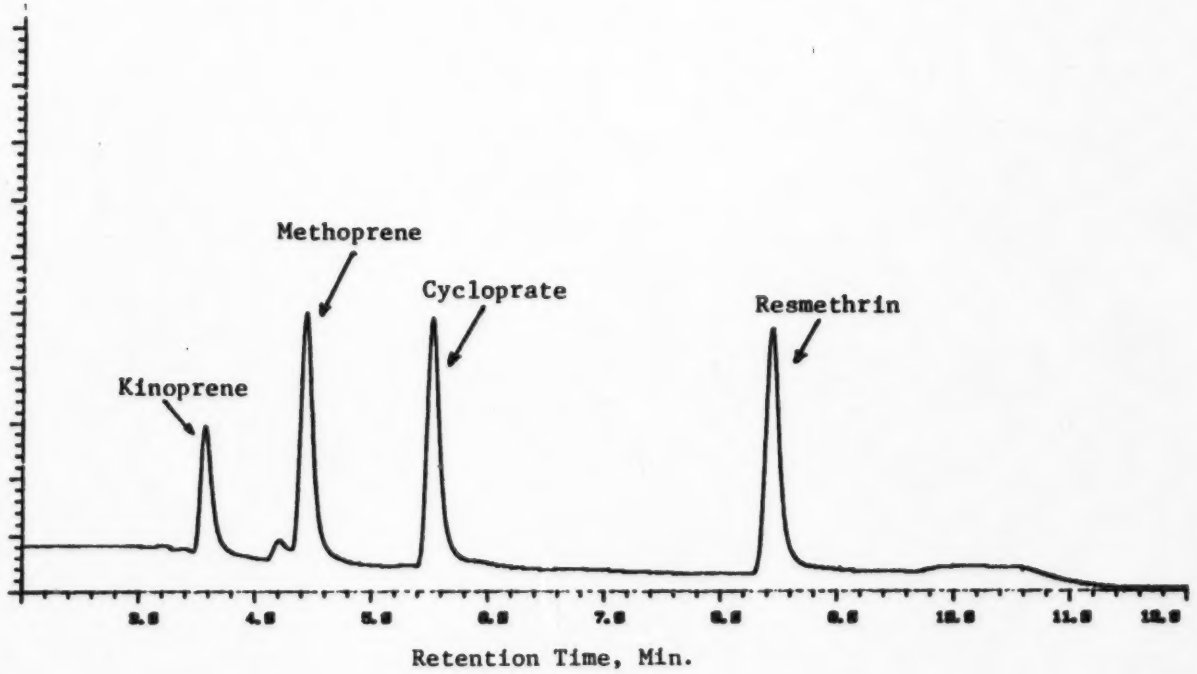


Figure 4.1. GC-FID Chromatogram of 200 ng each of C, H, and O Compounds (Column 1).

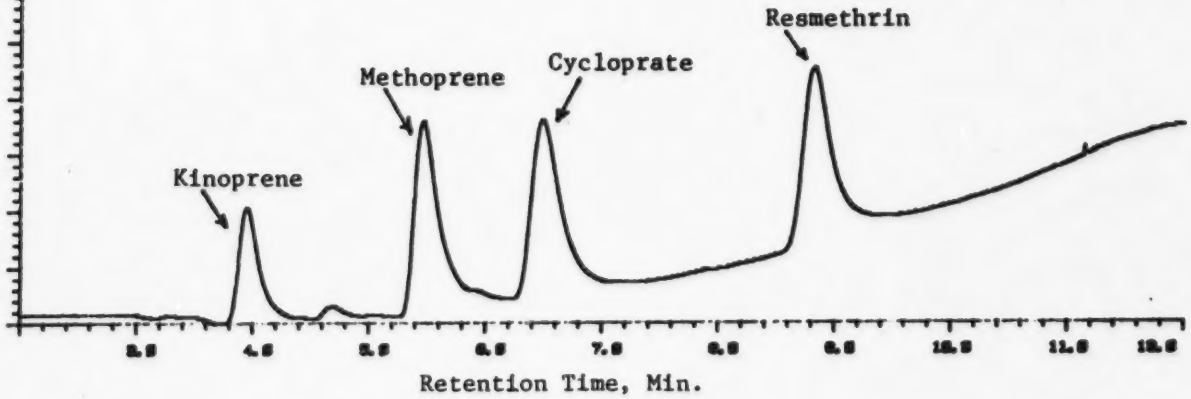


Figure 4.2. GC-FID Chromatogram of 200 ng each of C, H, and O Compounds (Column 2).